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Novel Deep Eutectic Solvent-based Vortex-Assisted Dispersive Liquid–Liquid Microextraction of Sm from End-of-Life Sm-Co Permanent Magnets and A Green Analytical Metrics Assessment

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Rare earth elements are important for sustainable technologies and their recovery from waste Sm-Co magnets is essential to reduce supply shortages. Quantitative samarium analysis is therefore vital for recycling workflows in sustainable e-waste management. Herein, we propose a green, vortex-assisted dispersive liquid-liquid microextraction method employing a novel hydrophobic deep eutectic solvent to preconcentrate samarium ions. Waste Sm-Co magnets were leached in 3 M HNO_3 to solubilize Sm ions, which were subsequently complexed at pH 5.0. The Sm-ARS (Alizarine red S) complex was extracted into a eugenol-based hydrophobic DES, with vortex agitation at 2800 rpm ensuring efficient phase separation. Quantification of the enriched analyte was performed *via* UV-Vis spectrophotometry at 590 nm. Experimental parameters including pH, λ_{max}, extraction duration, volume of chelating agent, extraction solvent volume and their type, centrifuge speed, interfering foreign ions, *etc*. was analyzed. These parameters were systematically optimized and the analytical figures of merit, such as the limit of quantification (6.26 µg/L), limit of detection (1.87 µg/L) and enrichment factor (40), were investigated under optimal experimental conditions. This methodology provides a sustainable, high-performance alternative to conventional extraction procedures. The environmental profile was rigorously appraised using the analytical eco-scale, the green analytical procedure index, the analytical GREEnness metric and the blue applicability procedure index. These results affirm the approach as a robust, sustainable alternative solution to conventional extraction procedure for the precise quantification of samarium.

Keywords: Deep eutectic solvent, Vortex-assisted dispersive liquid-liquid microextraction, Samarium, Sm-Co magnet.

INTRODUCTION

Rare earth elements play an important role in modern technologies due to their distinctive properties, particularly their strong magnetic behaviour and high energy density [1]. They are widely used in electronic devices and industrial applications, such as mobile phones, LED bulbs, display screens, televisions, permanent magnets, automobile catalysts and wind turbines [2]. China holds the largest share of global rare earth reserves, which account approximately 48.4% of the world's total reserves [3]. The rising demand for these elements has raised concerns about future supply shortages, market price fluctuations and geopolitical issues [4]. Recycling rare earth elements from discarded materials, such as waste electronic devices and spent magnets, offers a practical way to reduce dependence on primary resources. Spent Sm-Co magnets are particularly valuable due to their composition, which typically contains 46-61% cobalt, 32-39% samarium, 0.2-14% iron, 0.01-6% copper and 0.1-2% zirconium, along with other impurities [5]. The recovery of samarium and cobalt from these magnets has attracted considerable interest, as Sm-Co magnets are widely used in electric motors, wind turbines and medical equipment [6,7]. Their recycling offers an opportunity to recover valuable metals, improve the utilization of magnet waste and address the growing demand for cobalt and samarium. Accurate analysis and estimation of these elements in waste Sm-Co magnets are important steps towards developing effective recovery processes and increasing the economic value of magnet scrap [8].

Among the various separation techniques, solvent extraction is widely regarded as the industry-preferred and most effective method for the selective recovery as well as estimation of transition metals and rare earth elements from secondary resources, which offer product purity and scalability without the need for complex equipment. Traditional solvent extraction methods use large amounts of organic solvents, causing environmental problems and requiring more time and effort [9]. To address these limitations, the field of analytical chemistry has

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shifted toward sustainable, miniaturized alternatives that prioritize reagent efficiency and reduced processing complexity [10]. Several alternative techniques have been developed, such as dispersive liquid-liquid microextraction (DLLME) [11], cloud point extraction [12], solid-phase microextraction [13], liquid-phase microextraction [14], solid floating organic drop microextraction [15] and hollow fibre-based microextraction [16]. These methods reduce solvent use and simplify experimental procedures, making them more eco-friendly.

Dispersive liquid-liquid microextraction (DLLME), introduced by Rezaee *et al*. [17], is a rapid and efficient sample preparation technique used with spectrometric and chromatographic methods to enrich organic and inorganic analytes from aqueous samples. It involves the rapid injection of an extraction solvent mixed with a disperser solvent into an aqueous sample, forming a cloudy suspension of fine extractant droplets. The extraction phase is separated by centrifugation [18,19]. Rare earth elements (REEs) are commonly determined using inductively coupled plasma-mass spectrometry (ICP-MS) [20], inductively coupled plasma-optical emission spectrometry (ICP-OES) [21] and ICP-quadrupole mass spectrometry (ICP-QMS) [22]. UV-Vis spectrophotometry offers a simpler alternative for metal determination [23], although its application to REEs remains limited by sensitivity, matrix interference and sample pretreatment requirements. Conventional DLLME methods frequently use hazardous and volatile organic solvents, particularly halogenated compounds, raising environmental and safety concerns [24].

Hydrophobic DES (HDES) have also received increasing attention for extracting analytes from aqueous samples [25]. Van Osch *et al*. [26] reported water-immiscible eutectic mixtures based on decanoic acid and quaternary ammonium salts. Despite these developments, DES-based DLLME remains less explored for elemental determination than for organic compounds in food, water and biological samples [27-30]. High viscosity, matrix effects and compatibility with analytical instruments remain important limitations [31]. Research on DES and REEs has mainly focused on metal leaching and recovery, such as Nd/Fe and Sm/Co separation using Aliquat 336-glycerol eutectics and REE extraction using trioctylphosphine oxide-based systems [32,33]. By comparison, the analytical microextraction of REEs has largely relied on conventional extractants, with ICP-based techniques commonly used for quantification [34].

Eugenol-based hydrophobic DES have shown potential as extraction media. A eugenol-quaternary ammonium eutectic has been used in vortex-assisted DLLME coupled with UV-Vis spectrophotometry for copper determination in waste printed circuit boards [23]. Other HDES-based microextraction methods have targeted organic compounds such as rhodamine B, Allura red and Sudan dyes [35,36]. These solvents offer relatively simple preparation, low volatility and potential biodegradeability, making them suitable alternatives to hazardous organic solvents [37]. In present study, eugenol was selected as the hydrogen bond donor and combined with different quaternary ammonium salts to prepare hydrophobic DES for Sm(III) extraction. Variation in DES composition provides an opportunity to adjust solvent properties and metal-solvent interactions. To the best of our knowledge, eugenol-quaternary ammonium eutectics have not previously been applied to the microextraction and spectrophotometric determination of samarium.

Vortex-assisted DLLME (VA-DLLME) [38] offers a simple approach to improving extractant dispersion and extraction efficiency. The present method uses a vortex mixer to disperse the hydrophobic DES rapidly in the aqueous sample without requiring an additional disperser solvent. This method is particularly relevant to trace-level samarium determination, where preconcentration is necessary to achieve adequate analytical sensitivity [39]. The environmental performance of an analytical method should be assessed through appropriate evaluation tools rather than inferred solely from the solvent used. Common assessment methods include the Analytical Eco-Scale (AES) [40], Green Analytical Procedure Index (GAPI) [41], Analytical GREEnness metric (AGREE) [42] and Blue Applicability Grade Index (BAGI) [43]. Although DES-based extraction has been widely investigated for organic compounds and REE recovery, its application to the analytical determination of samarium in spent Sm-Co magnets remains insufficiently explored. The present study addresses this gap by combining eugenol-based HDES with VA-DLLME and UV-Vis spectrophotometry for the extraction, detection and quantification of Sm(III) in waste Sm-Co magnet waste. The proposed method aims to provide a simple, rapid and cost-effective alternative to conventional solvent-intensive procedures. Its environmental performance and practical applicability are evaluated using AES, GAPI, AGREE and BAGI.

EXPERIMENTAL

Certified Samarium standard solution (1000 mg/L), obtained from Sigma-Aldrich (India), was used to prepared standard stock solution. The stock solution was serially diluted with double-distilled water to prepare standard Sm(III) solutions at the required concentrations (µg/mL). Eugenol and Alizarin Red S dye were purchased from Loba Chemicals (India), while quaternary ammonium salts were obtained from Spectrochem (Mumbai, India). All other analytical-grade chemicals and solvents were supplied by S.D. Fine-Chem (Boisar, India). Double-distilled water used throughout the experimental work.

Synthesis of DESs: Deep eutectic solvents (DESs) are eco-friendly alternatives to conventional solvents, offering simple preparation, low cost and low volatility. Their formation from quaternary ammonium salts and eugenol provides useful solvation properties for selective Sm^{3+} extraction by DLLME. In this study, a series of six quaternary ammonium salts *viz*. (i) benzyl triethyl ammonium chloride, (ii) benzyl triethylammonium bromide, (iii) benzyl trimethylammonium chloride (BTMAC), (iv) benzyl trimethylammonium bromide, (v) benzyl tributylammonium chloride and (vi) benzyl tributylammonium bromide, were combined with eugenol to synthesize the hydrophobic deep eutectic solvents. The selected DESs were prepared using 3:1 molar ratio of eugenol to salt. The reactants were accurately weighed into a glass vessel and magnetically stirred at 55 ºC until a clear, the resulting homogenous stable liquid was produced, which was subsequently allowed to cooled to ambient temperature and subjected to further analysis.

Instruments: A UV-Vis spectrophotometer (UV-1800, Shimadzu, India) was used for absorbance measurements. Sample mixing, phase separation and pH monitoring were carried out using a vortex mixer (Remi, India), centrifuge (Remi, India) and pH meter (Thermo Scientific, India), respectively. The Sm-Co magnets scraps was leached using a digital rota mantle (Remi, India).

VA-DLLME of Sm(III): Before analysis, the sample was preconcentrated in a 15 mL calibrated conical tube. A 10 mL aqueous solution containing 118 µg/L Sm(III) was mixed with 200 µL of 0.06% (w/v) Alizarin Red S (ARS) at pH 5.0 to form the Sm-ARS complex. The complex was extracted by rapidly injecting 250 µL of eugenol-benzyltrimethylammonium chloride hydrophobic DES using a syringe. The mixture was vortexed at 2800 rpm for 1 min to disperse the DES into fine droplets, forming a cloudy suspension. The extractant phase was then separated by centrifugation at 4800 rpm. The sedimented phase was collected using a syringe and directly analyzed by UV-Vis spectrophotometry using a 1 mL microcuvette. The fine DES droplets provide a large contact area, improving analyte extraction and preconcentration.

Analysis of real samples: Spent Sm-Co magnet samples were obtained from Sonal Magnetics (Gujarat, India). Four samples weighing 1.308, 1.305, 1.315 and 1.291 g were selected for leaching. Each sample was treated with 30 mL of 3 M nitric acid in a 250 mL round-bottom flask at 60 ºC for 1 h under stirring at 560 rpm using a digital rota mantle. An exothermic reaction during dissolution increased the temperature to approximately 80 ºC. After cooling, the solution was filtered through Whatman filter paper and the filtrate was diluted to 1000 mL with double-distilled water. An aliquot was further diluted to 100 mL before samarium determination using the VA-DLLME method.

Greenness evaluation of DLLME of samarium: The environmental performance of the proposed method was evaluated using established green analytical metrics, for example, the Analytical Eco-Scale (AES) [44], AGREE [42], AGREE-prep [45] and Blue Applicability Grade Index (BAGI) [43]. These tools assess reagent consumption, energy use, waste generation and operator safety, providing a comprehensive evaluation of the method's sustainability and practical applicability.

RESULTS AND DISCUSSION

Eugenol (4-allyl-2-methoxyphenol) was selected as the hydrogen-bond donor (HBD) due to the presence of a phenolic hydroxyl group, which can interact with the hydrogen bond acceptor (HBA). Its aromatic ring and allyl group contribute to the hydrophobic character of the eutectic phase, while the methoxy and allyl substituents may influence molecular packing and the physico-chemical properties of the solvent. The hydrophobic character of the resulting DES facilitates the partitioning of the Sm-ARS complex from the aqueous phase into the extraction phase.

Benzyltrimethylammonium chloride (BTMAC) was chosen as the hydrogen-bond acceptor (HBA). The chloride anion serves as the primary hydrogen-bond acceptor by interacting with the phenolic hydroxyl group of eugenol. The benzyltrimethylammonium cation contributes to the solvent framework and its hydrophobic character. Interactions between eugenol and BTMAC govern the molecular structure of the DES and may influence its phase behaviour and extraction efficiency. The partitioning of the Sm-ARS complex into the DES phase is governed by its chemical speciation, DES composition and experimental conditions.

FTIR analysis provided evidence of the intermolecular hydrogen bonding during DES formation. The O–H stretching band shifted from approximately 3500 cm^{-1} in pure eugenol to 3300-3100 cm^{-1} in the DES formulations, accompanied by band broadening, which is consistent with hydrogen bond formation (Fig. 1). The ^{1}H NMR spectra examined for characteristic proton chemical shifts associated with intermolecular interactions (Fig. 2). TGA was conducted using a 10 mg sample over 25-400 ºC at a heating rate of 10 ºC min^{-1} under nitrogen flow (40 mL min^{-1}) to assess thermal stability and moisture loss (Fig. 3). The sample undergoes a slight weight loss of 2.43% up to 105 ºC followed by a sharp decrease of 97.49% between 105 and 330.53 ºC due to the thermal decomposition of the DES. These analyses support the formation and physico-chemical characterization of the synthesized DESs and their potential suitability as extraction phases in VA-DLLME.

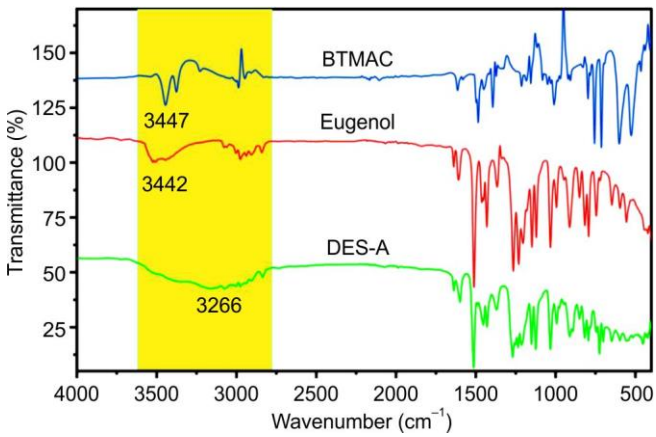


Fig. 1. Comparative FTIR spectra of eugenol, BTMAC and eugenol-BTMAC deep eutectic solvent

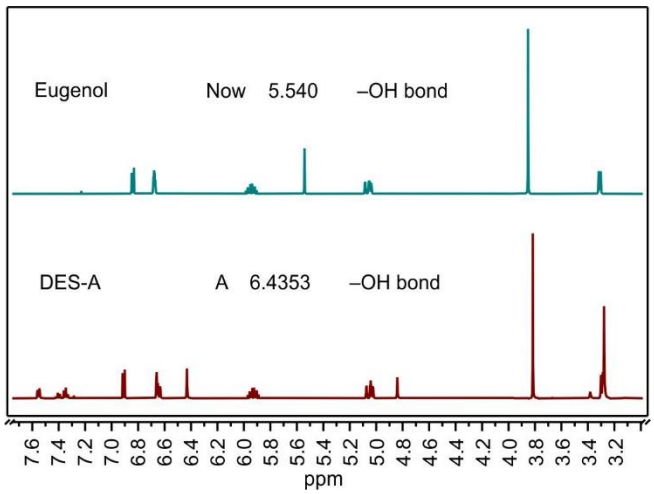


Fig. 2. ^{1}H NMR spectra of pure eugenol and eugenol-BTMAC deep eutectic solvent

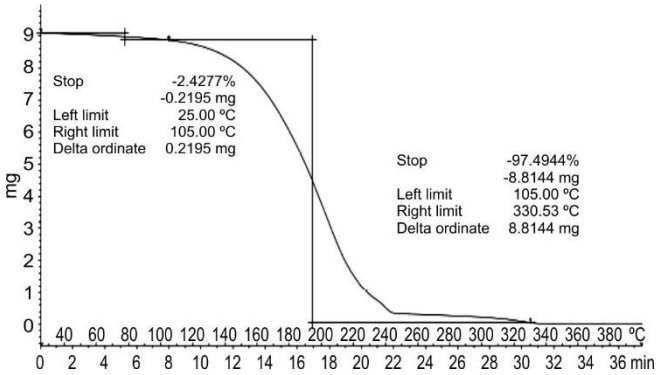


Fig. 3. Thermogram of eugenol-BTMAC deep eutectic solvent

Optimization of extraction parameters: The developed method offered rapid and efficient extraction, although optimization of the experimental conditions was necessary to achieve reliable analytical performance. The effects of pH, chelating reagent concentration and volume, extraction solvent selection and volume, vortexing time, centrifugation conditions, salt addition and foreign-ion interference were investigated. These parameters were assessed to establish suitable extraction conditions and improve the method's performance. The extraction recovery (ER) and enrichment factor (EF) were used as key measures of extraction efficiency. Both parameters were calculated using Eqs. (1) and (2), respectively [46,47]:

$$\text{Recovery (\%)} = \frac{C_{des}}{C_o} \times 100 \quad (1)$$

$$\text{Enrichment factor} = \frac{V_{sample}}{V_{sediment}} \quad (2)$$

where C_{des} and C_o are the concentrations of the analyte in the DES phase after extraction to the original analyte concentration; V_{sample} and $V_{sediment}$ are the volumes of sample and sedimented phase, respectively.

Absorption spectra: The absorption spectra of the Sm-ARS complex before and after VA-DLLME were recorded using a UV-Visible spectrophotometer to examine the extraction behaviour and establish the analytical wavelength. As shown in Fig. 4, the complex exhibited a distinct absorption maximum at approximately 590 nm. The absorbance increased from approximately 0.12 before extraction to 0.64 after VA-DLLME. This enhancement in absorption intensity is consistent with the enrichment of the Sm-ARS complex in the DES phase. The wavelength of 590 nm was selected for subsequent quantitative measurements. All measurements were performed against a reagent blank.

Effect of pH: The pH of the sample solution plays an important role in the formation and extraction of the Sm-ARS complex during VA-DLLME. The effect of pH on extraction recovery was investigated over the range of 2.09-9.0, with adjustments made using 0.1 mol L^{-1} HCl and NaOH. The extraction recovery increased as the pH rose from 2.0 to 5.0, reaching maximum values within the pH range of 5.0-6.0 (Fig. 5). At lower pH values, protonation of ARS may limit its interaction with samarium ions, while suitable pH conditions favour complex formation and extraction. A pH of 5.0 was selected for subsequent experiments.

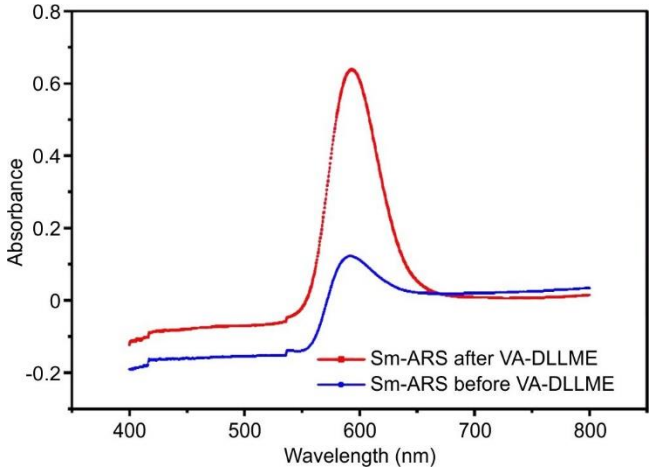


Fig. 4. Absorption spectra for Sm-ARS complex after and without VA-DLLME [conditions: λ_{max}: 590 nm, Sm(III) ions: 118 μg/L, ARS-0.06% w/v, vortex: 2800 rpm/min, DES: 250 μL]

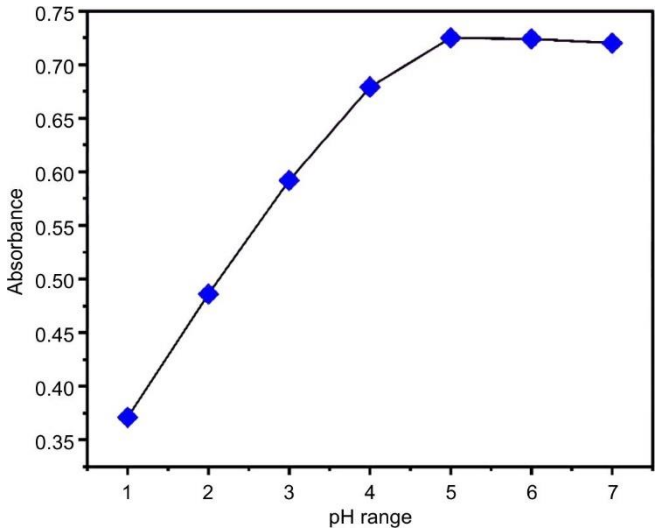


Fig. 5. Effect of pH on absorption of Sm-ARS complex [conditions: λ_{max}: 590 nm, Sm(III) ions: 118 μg/L, ARS: 0.06% w/v, vortex: 2800 rpm/min, DES: 250 μL]

Effect of amount of ARS (chelating reagent): The concentration of ARS was optimized to establish the amount required for effective complexation with Sm(III) ions. ARS concentrations ranging from 0.01% to 0.1% were examined. The absorbance increased with increasing ARS concentration up to 0.06%, beyond which no appreciable improvement was observed (Fig. 6a). Accordingly, 0.06% ARS was selected for subsequent experiments. The volume of the ARS solution was then varied from 50 to 350 μL to assess its influence on extraction recovery. The recovery of Sm increased with reagent volume and reached a plateau at approximately 200 μL (Fig. 6b). A volume of 200 μL was selected as the optimum amount for Sm-ARS complex formation and subsequent extraction.

Selection of DES: The choice of extraction solvent is an important factor governing the recovery of the target analyte from the sample matrix. Several hydrophobic deep eutectic solvents (DESs) were evaluated for their extraction performance. Among the solvents tested, DES-C provided the

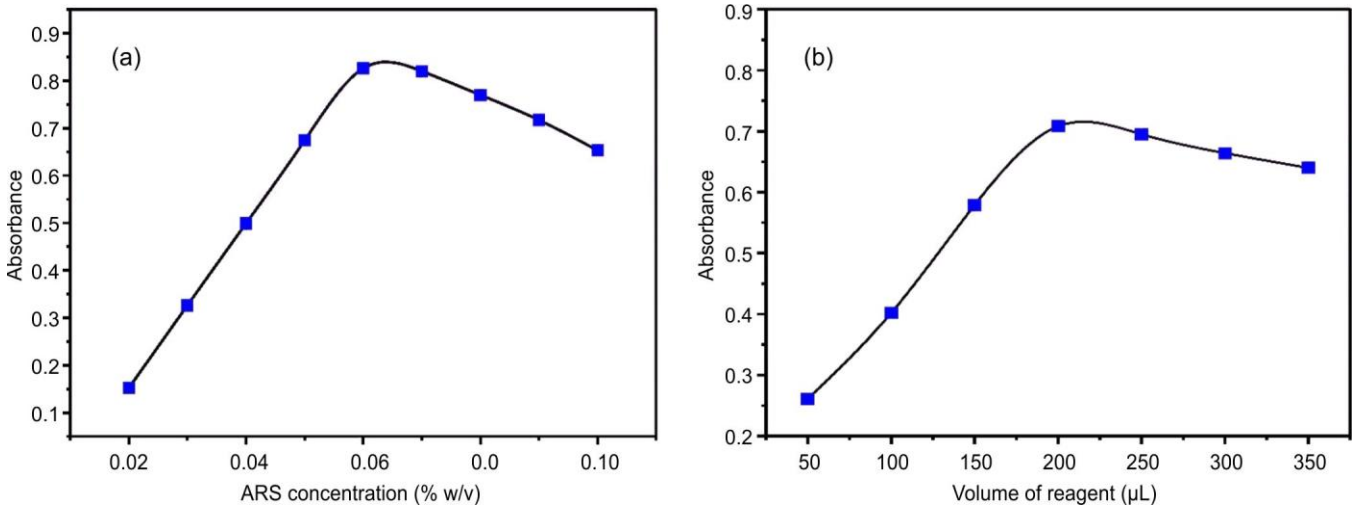


Fig. 6. (a) Optimizing the concentration of chelating reagent ARS and (b) the volume of chelating reagent ARS [conditions: λ_{max}: 590 nm, Sm(III) ions: 118 µg/L, pH: 5.0, ARS: 0.06% w/v, vortex: 2800 rpm/min]

highest extraction efficiency and was selected for further optimization. The effect of DES-C volume was examined over the range of 25-400 µL under the optimized experimental conditions. Extraction recovery increased with solvent volume and reached its maximum at 250 µL (Fig. 7). This volume was selected for subsequent experiments to achieve efficient extraction while limiting solvent consumption.

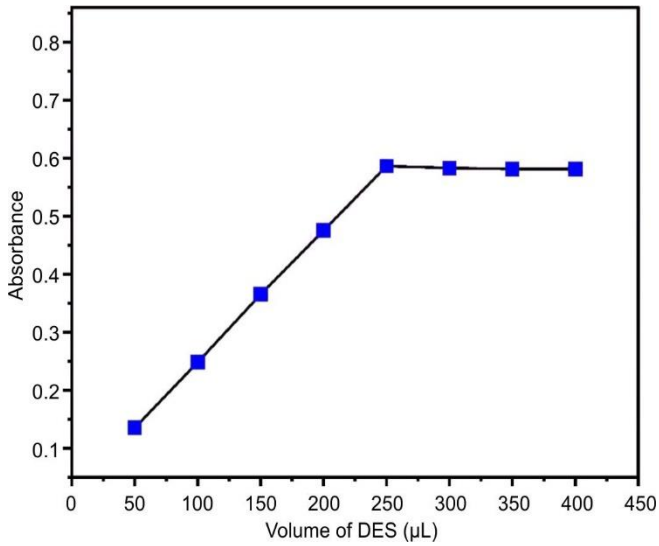


Fig. 7. Optimizing the volume of extraction solvent [conditions: λ_{max}: 590 nm, Sm(III) ions: 118 µg/L, pH: 5.0, ARS: 0.06% w/v, vortex: 2800 rpm/min]

Effect of vortex time: The effect of vortexing time was examined over the range of 10-90 s, while keeping the other experimental conditions optimized. The extraction efficiency, assessed through absorbance measurements, increased with vortexing time up to 60 s, beyond which no appreciable change was observed (Fig. 8). This plateau indicates that sufficient dispersion and mass transfer had been achieved within 1 min. A vortexing time of 60 s was selected for subsequent experiments, providing adequate extraction within a short processing time.

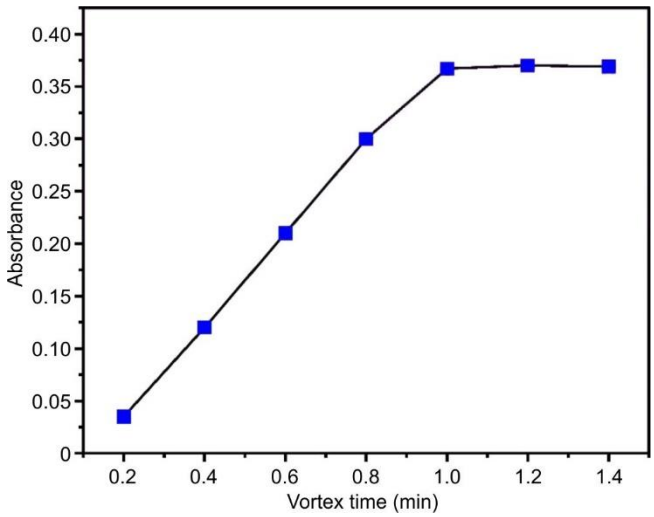


Fig. 8. Optimized the volume of vortex time [conditions: λ_{max}: 590 nm, Sm(III) ions: 118 µg/L, pH- 5.0, ARS: 0.06% w/v, vortex: 2800 rpm/min]

Optimization of centrifugation conditions: Following vortex agitation at 2800 rpm, the Sm-ARS complex was transferred into the DES phase under the optimized extraction conditions. Centrifugation was performed to facilitate phase separation and obtain the Sm-enriched DES phase. The centrifugation speed and duration were optimized, with 4800 rpm for 1 min providing effective separation. Under these conditions, the DES phase accumulated at the bottom of the centrifugation tube, allowing its convenient recovery using a syringe. The isolated phase containing the Sm-ARS complex was subsequently subjected to UV-Visible spectrophotometric analysis. The selected centrifugation conditions provided rapid and effective phase separation for subsequent analysis.

Effect of addition of salt: The effect of salt addition on the extraction efficiency of samarium was examined using different concentrations (2.5%, 5% and 10%) of NaCl, KCl, Na_2SO_4 and $NaNO_3$. The experiments were conducted using a samarium solution of 118 µg L^{-1} under the optimized extraction conditions. Salt addition was investigated to assess

whether the salting-out effect could improve the transfer of the Sm-ARS complex into the DES phase by reducing its solubility in the aqueous medium. The results revealed that none of the tested salts enhanced the extraction efficiency compared with the salt-free system. Accordingly, further experiments were also performed without adding salt to the sample solution.

Mechanism of Sm^{3+} extraction: The extraction of Sm-ARS complex from the aqueous phase into the hydrophobic eugenol-BTMAC DES involves several interactions. The phenolic hydroxyl group of eugenol participates in hydrogen bonding with donor sites on the chelate, while the hydrophobic character of the HDES and dispersion forces favour solvation of the transferred species. Interactions involving aromatic ring of eugenol also contribute to the stability of the metal-ligand complex within the HDES medium. Together, combined effects of hydrogen bonding, interfacial on pairing and hydrophobic partitioning rationalize the extraction of the Sm-ARS species into the HDES phase. A standard 1:2 metal to ligand stoichiometry in the presence of excess ligand, the equilibrium can be expressed as follows [48]:

$$Sm^{3+} + 2HL^{2-} \rightleftharpoons [Sm(L_2)]^- + 2H^+ \quad (3)$$

$$M + L \rightarrow M\text{-}L + DES \rightarrow M\text{-}L\text{-}DES$$

where M = metal, L = complexing reagent, DES = deep eutectic solvent.

At pH 5.0, Sm^{3+} coordinates with oxygen-donor sites on Alizarin red S, potentially displacing water molecules from its hydration sphere. The anionic Sm-ARS complex may relate electrostatically with the BTMAC cations at the aqueous-HDES interface through interactions involving the sulphonate groups. This association can reduce the effective charge and hydration of the complex, which favour its transfer into the hydrophobic phase. Similar anion-exchange mechanisms have been reported in quaternary ammonium-based eutectic systems [49]. The extraction process may involve three successive steps: (i) formation of the Sm-ARS complex in the aqueous phase, (ii) interfacial association with BTMAC cations and (iii) subsequent partitioning into the HDES phase. Vortex-assisted agitation promotes the dispersion of HDES into fine droplets, increasing the interfacial area and reducing diffusion distances. These conditions facilitate mass transfer and enable rapid extraction without the use of an auxiliary dispersing solvent.

Effect of metal interference: The influence of the co-existing ions on Sm(III) extraction was examined to assess the selectivity of the proposed VA-DLLME method in complex sample matrices. Solutions containing 118 μg L^{-1} Sm(III) were spiked with different concentrations of potential interfering ions and subjected to the optimized extraction procedure. The recovery values are shown in Table-1. The formation of the Sm-ARS complex, with its characteristic absorption maximum at 590 nm, provides the basis for spectrophotometric determination. The presence of the tested foreign ions had little effect on extraction performance, with recoveries remaining above 98% under the investigated conditions. Fe(III) interference at moderate concentrations was effectively controlled by the addition of thiocyanate as a masking agent. The recovery results support the applicability of the proposed method for Sm(III) determination in samples containing different coexisting ions.

TABLE-1
INTERFERENCE EFFECT OF SOME MATRIX IONS ON PERCENT RECOVERIES OF Sm(III), pH: 5, VOLUME OF SAMPLE: 10 mL, ARS: 0.06% w/v, DES: 250 μL (RELATIVE ERROR ± 5%)

Metal interference	Proportion	Recovery (%)
Cu(II)	1:400	98.2
[a]Ni(II)	1:120	92.1
Zn(II)	1:120	90.6
[b]Cr(VI)	1:120	90.2
Co(II)	1:200	104.7
[c]V(V)	1:120	91.2
Ca^{2+}	1:80	96.5
Mg(II)	1:80	96.7
Al(III)	1:80	97.7
Hg(II)	1:40	98.4
[a]Fe(III)	1:120	91.8
SO_4^{2-}	1:80	97.8
$S_2O_3^{2-}$	1:600	108.8
F^-	1:40	99.1
Cl^-	1:40	99.6
Br^-	1:400	109.5
I^-	1:40	96.5
NO_3^-	1:160	98.3
PO_4^{3-}	1:200	98.6

[a]Masked with 0.6 mg thiosulphate; [b]Masked with 0.7 mg oxalic acid; [c]Masked with thiourea.

Analytical figures of merit and validation of DES-VA-DLLME method: The analytical performance of the optimized DES-VA-DLLME method coupled with UV-Visible spectrophotometry was evaluated in terms of linearity, limits of detection (LOD), limits of quantification (LOQ), precision and enrichment factor (EF), following the relevant ICH guidelines. The calibration curve exhibited good linearity over the Sm(III) concentration range of 30-150 μg L^{-1}, with a correlation coefficient (R^2) of 0.9994. The intra-day precision, evaluated at 118 μg L^{-1} (n = 10), was 2.78% RSD. The LOD and LOQ were calculated as 1.87 and 6.26 μg L^{-1}, respectively, while the enrichment factor was 40. These analytical parameters establish the sensitivity, precision and enrichment capability of the method for Sm(III) determination. Its application to waste permanent magnet samples further supports its potential use in the analysis of complex matrices. The analytical figures of merit for the VA-DLLME method are shown in Table-2.

Comparison with reported methods: The present study describes a DES-based vortex-assisted dispersive liquid-

TABLE-2
CALIBRATION AND VALIDATION PARAMETERS OF THE PROPOSED ANALYTICAL METHOD

Parameter	Analytical figures
Determination coefficient (R^2)	0.9987
Linear Range	30-150 μg/L
Limit of detection (LOD*) (n = 10)	1.87 μg/L
Limit of quantification (LOQ*) (n = 10)	6.26 μg/L
Relative standard deviation (RSD) (n = 10)	2.78%
Enrichment factor	40

*LOD and *LOQ based on 3.3 and 10 σ criteria, respectively.

TABLE-3
COMPARATIVE ASSESSMENT OF SEPARATING AND ANALYTICAL TECHNIQUES FOR SAMARIUM AND OTHER REEs

Extraction/analytical technique	Sample matrix	Target analytes	Solvents	Ref.
DLLME/ICP-QMS	Ground water	14 REEs	Aliquat®336 (tricaprylmethylammoniumchloride)	[22]
Air-assisted cloud point extraction (AACPE)	Rock, industrial wastewater	Sm(III)	Triton X-114	[50]
FA-HLLME/ICP-MS	Mineral concentrate	Sm	1-Dodecanol/Acetone	[51]
D-SPE-DLLME/ETV-ICP-MS	Lake water, river water	14 REEs	Carbon tetra chloride	[52]
LL-DLLME/ICP-MS	Water samples	14 REEs	Acetone carbon tetra chloride	[53]
VA-DLLME/UV-Vis spectrophotometry	Waste Sm-Co magnet	Sm(III)	Eugenol-based HDES	Present work

ICP-OES: Inductive couple plasma optical emission spectroscopy, REE: Rare earth element, FA-HLLME: Floatation assistance homogenous liquid-liquid microextraction, ICP-QMS: Inductively coupled plasma-quadrupole mass spectrometry, ETV-ICP-MS: Electrothermal vaporization-inductively coupled plasma mass spectrometry.

liquid microextraction (DES-VA-DLLME) method coupled with UV-Visible spectrophotometry for the determination of samarium in waste Sm-Co magnets. The use of a hydrophobic deep eutectic solvent provides an alternative to conventional extraction systems that rely on hazardous organic solvents. The proposed method offers a linear working range of 30-150 μg L^{-1}, a limit of detection (LOD) of 1.87 μg L^{-1} and an intra-day precision of 2.78% RSD. These analytical characteristics support its application to trace-level Sm(III) determination in complex matrices. The analytical performance of the proposed method in comparison with previously reported extraction and determination techniques is shown in Table-3.

Applications of real sample: The developed DES-VA-DLLME procedure was applied to the determination of samarium in waste Sm-Co magnets collected from different wind turbine manufacturing sites. The spent magnets were digested using nitric acid to prepare stock solutions, which were subsequently analysed under the optimized extraction conditions. Samarium concentrations were determined using calibration curves prepared from aqueous standards subjected to the same DES-VA-DLLME procedure. Method accuracy was assessed through spiking experiments using the prepared sample solutions. The measured samarium concentrations agreed closely with the expected values. Four waste magnet samples of different masses were examined to assess the extraction performance. The spiked samarium concentrations were varied from 0 to 15 μg L^{-1}. The measured Sm concentrations increased proportionally with the added amount. Recovery values ranged from 99.0% to 100.5% (Table-4). These results confirm efficient samarium extraction from the digested magnet samples and support the accuracy and practical applicability of the proposed method for analyzing waste Sm-Co magnets.

Greenness and practicality evaluation of proposed methodology: Green analytical chemistry (GAC) provides guidelines for developing analytical procedures with reduced environmental impact. Particular attention is given to sample preparation as this stage often involves substantial solvent consumption and waste generation. The 12 principles of GAC encourage simplified analytical procedures with fewer preparation steps and reduced reagent consumption. They favour safer solvents and room-temperature operations to minimise energy requirements [54]. These practices support laboratory

TABLE-4
DETERMINATION OF SAMARIUM IN WASTE Sm-Co MAGNET

Waste Sm-Co magnet weight (g)	Samarium amount (μg/mg)		Recovery (%)
	Spiked	Found*	
Specimen A (1.308)	0	342.5 ± 0.15	–
	10	353.5 ± 0.35	100.28
	15	358.5 ± 0.35	100.28
Specimen B (1.305)	0	346.4 ± 0.24	–
	10	356.4 ± 0.49	100
	15	361.3 ± 0.36	99.97
Specimen C (1.315)	0	341.4 ± 0.51	–
	10	351.8 ± 0.13	100.11
	15	357.9 ± 0.20	100.42
Specimen D (1.291)	0	347.8 ± 0.49	–
	10	358.9 ± 0.05	100.31
	15	363.5 ± 0.11	100.19

*Mean ± standard deviation (n = 5)

safety and reduce operational costs while maintaining analytical performance. Among the available microextraction techniques DLLME [34] offers an alternative to conventional liquid–liquid extraction and solid-phase extraction through lower solvent consumption and reduced exposure to hazardous chemicals [55]. The use of centrifugation in the present procedure remains a limitation for complete automation. Sample matrix composition and analyte stability can influence extraction efficiency and the reliability of the final results. The environmental performance and practical applicability of the proposed DES-VA-DLLME procedure were assessed using four complementary evaluation tools. These included the analytical eco-scale (AES) and green analytical procedure index (GAPI) as well as the analytical GREEnness metric approach (AGREE) and blue applicability grade index (BAGI). These tools examine different aspects of analytical sustainability through chemical hazards and environmental impact as well as solvent consumption and waste generation.

The analytical eco-scale (AES) provides a semi-quantitative assessment of the environmental impact of an analytical procedure. It starts with a reference score of 100 from which penalty points are deducted according to reagent type and quantity. Chemical hazards and energy consumption are considered along with occupational risks and waste generation. The final score is classified as excellent green

(>75 points) or acceptable green (50-75 points) or inadequate green (<50 points) [40]. The optimized vortex-assisted DLLME procedure for Sm(III) determination achieved an AES score of 86 with a total of 14 penalty points (Table-5). This score places the proposed method in the excellent green category. The favourable score is consistent with the reduced use of conventional organic extraction solvents and the relatively low solvent consumption associated with the microextraction procedure. The high samarium recovery further supports its analytical suitability as an alternative approach for rare earth element determination.

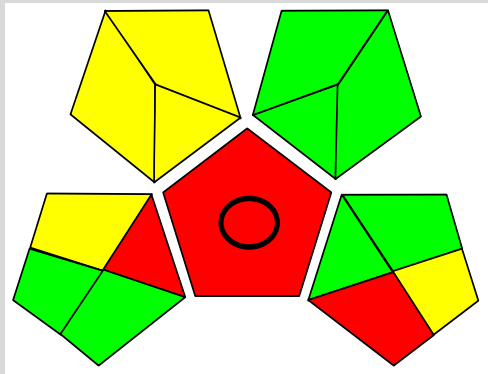
The green analytical procedure index (GAPI) provides a visual assessment of the environmental impact associated with different stages of an analytical procedure through a colour-coded pictogram [56]. The GAPI pictogram presented in Table-6 contains seven green segments and three red segments. The green segments represent operations with favourable environmental characteristics while the red segments

TABLE-5
THE GREENNESS PROFILE OF THE HDES-VA-DLLME METHOD AS DETERMINED BY USING THE ANALYTICAL ECO-SCALE TOOL

Items				Penalty points (PPs)
Reagents	Alizarine red S	Amount	<10 mL	1
		Hazard type	Signal word: warning	1
		Hazard amount	1 Pictogram	1
				Total PPs = 2
	BTMAC	Amount	<10 mL	1
		Hazard type	Signal word: Danger	2
		Hazard amount	1 Pictogram	1
				Total PPs = 3
	Eugenol	Amount	<10 mL	1
		Hazard type	Signal word: warning	1
		Hazard amount	1 Pictogram	1
				Total PPs = 2
Instruments	Energy (kWh per sample)	UV-Vis spectrometry	≤ 0.1	0
		Vortex Mixer	≤ 0.1	0
		Centrifugation	1 min @ 4800 rpm	1
	Occupational hazard		No hermetic sealing release of gas or vapour into air	0
				Total PPs = 1
Waste	Waste amount		1-10 mL	3
	Waste treatment		No treatment	3
				Total PPs = 6
Total penalty points	Eco-Scale score			100 – 14 = 86

TABLE-6
THE GREENNESS PROFILES OF THE DEVELOPED METHOD USING THE GAPI TOOL

Sample preparation	
Collection (1)	Offline (red)
Preservation (2)	None (green)
Transport (3)	None (green)
Storage (4)	Under Normal conditions (yellow)
Type of method	
Direct or indirect (5)	Extraction required (red)
Scale of extraction (6)	Micro-extraction (yellow)
Solvents/reagents used (7)	Green solvents (yellow)
Additional treatments (8)	Simple treatments (yellow)
Reagent and solvents	
Amount (9)	< 10 mL <10 g) (Green)
Health hazard (10)	Slightly toxic, slight irritant; NFPA health hazard score of 0 or 1. No special hazards (green)
Safety hazard (11)	Highest NFPA flammability or instability score of 0 or 1. No special hazards (green)
Instrumentation	
Energy (12)	<=0.1 kWh per sample (green)
Occupational hazard (13)	Hermetic sealing of the analytical process (green)
Waste (14)	1-10 mL (1-10g) (yellow)
Waste treatment (15)	No treatment (red)



identify stages associated with a higher environmental burden. This distribution provides a stage-wise assessment of the procedure and identifies areas where further improvement may be possible. The proposed method supports both qualitative and quantitative determination of samarium. The GAPI assessment provides useful information on the environmental characteristics of the complete analytical workflow.

The analytical GREEnness metric approach (AGREE) was applied as a third tool to evaluate the method against the 12 principles of green analytical chemistry. This approach provides a numerical score ranging from 0 to 1 [42]. The proposed DES-VA-DLLME method achieved an AGREE score of 0.65 as shown in Table-7. This value supports its favourable greenness profile. The use of a hydrophobic deep eutectic solvent reduces dependence on conventional hazardous organic extraction solvents. The microextraction procedure limits solvent consumption and reduces waste generation during sample preparation. These features contribute to the environmental performance of the proposed method during samarium determination using UV-Visible spectrophotometry.

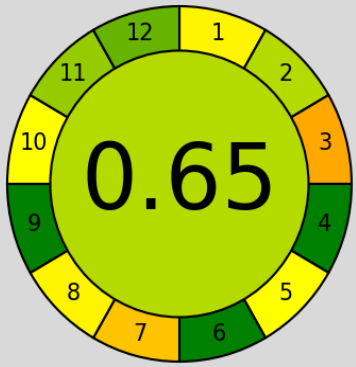
The blue applicability grade index (BAGI) was employed to assess the practical suitability of the proposed method within the framework of white analytical chemistry [43]. Unlike the greenness assessment tools BAGI focuses on analytical applicability and operational performance. It evaluates the technical suitability of an analytical procedure and its fitness for the intended application. The proposed method achieved a BAGI score of 62.5, which exceeds the specified acceptance threshold of 60. The corresponding pictogram displays a favourable distribution of light-blue zones as shown in Table-7. This score supports the practical applicability of the procedure and its potential use in routine samarium determination. The BAGI assessment provides a complementary perspective to the environmental evaluation obtained through AES and GAPI.

The four assessment tools provide information on the environmental performance and practical suitability of the proposed DES-VA-DLLME procedure. The AES score of 86 places the method in the excellent green category while the AGREE score of 0.65 supports its environmental suitability. The GAPI pictogram provides a visual assessment of the individual analytical stages while the BAGI score of 62.5 supports its practical applicability (Table-8). The use of a hydrophobic deep eutectic solvent and a low-volume extraction procedure offers an alternative approach to samarium determination in waste Sm-Co magnets with reduced reliance on conventional organic extraction solvents. These findings support the environmental and analytical potential of the proposed method for rare earth element analysis.

Conclusion

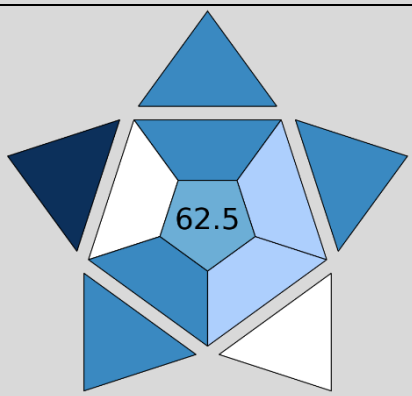
The present study establishes a DES-based vortex-assisted dispersive liquid–liquid microextraction (DES-VA-DLLME) procedure coupled with UV-Visible spectrophotometry for the determination of samarium in waste Sm-Co magnets. A proposed formulated eugenol-based hydrophobic deep eutectic

TABLE-7
GREENNESS EVALUATION OF THE DEVELOPED METHOD USING THE (a) AGREE AND (b) BAGI TOOLS



(a) AGREE pictogram

1	Sample treatment: Offline analysis
2	Sample size: 1.0 g
3	Position of the analytical device: At line
4	Sample preparation steps: 3
5	Automation and miniaturization: Manual/non or miniaturized
6	Derivatization: No derivatization
7	Amount of waste: 10 mL
8	Analysis throughput: 1 analyte, 9 samples per hour
9	Energy consumption: UV-Vis spectrophotometer – 0.1kWh
10	Types of reagents: some reagents are bio-based
11	Toxicity: yes, 0.2 mL
12	Safety: Toxic to aquatic life



(b) BAGI pictogram

1	Types of analysis: Quantitative
2	Multi or single-element analysis: Single-element
3	Analytical technique: Simple instrumentation available in most labs (spectrophotometry)
4	Simultaneous sample preparation: 2-12
5	Sample preparation: Miniaturized extraction sample preparation (DLLME)
6	Samples per h: 5-10
7	Reagents and materials: Common commercially available reagents
8	Preconcentration: Preconcentration required. Required sensitivity is met with one-step preconcentration
9	Degree of automation: Manual treatment and analysis
10	Amount of sample: <10 mL (or g) environmental samples

TABLE-8
COMPARATIVE OVERVIEW OF THE ANALYTICAL PERFORMANCE AND GREEN CHEMISTRY CHARACTERISTICS OF THE PROPOSED HDES-VA-DLLME METHOD AND SELECTED ESTABLISHED EXTRACTION METHODS

Extraction methods/ Solvent system	DES composition	Disperser solvent required	Target analytes/ Recovery (%)	Green metric tool score/profile	Ref.
SFODME	Morin + 1-undecanol	–	Y, Sm, Eu, Gd, Er, Yb	Not reported	[15]
Chelate DLLME	Tetrachloroethylene + D2EPHA	Acetone	14 REEs/61-109%	AGREE: 0.61 Eco-Scale: 26.6-79.8 GAPI: 6 red fields	[34]
Surfactant-based DES-DLLME	Triton X-114 + Ethylene glycol HDES	None	Rhodamine-B, Allura red 96.5-99.6%	AGREE 0.78 BAGI 70	[35]
LL-DLLME	CCl_4	Acetone	REE/94-124%	Not reported	[53]
Conventional solvent extraction	Organophosphorus (D2EHPA in kerosene)	None (batch LLE)	Rare earths/80-95%	Not reported	[57]
Hydrophilic DES-DLLME	Type III (choline chloride:urea; 1:2)	Not applicable	Transition metals/93-105%	Not reported	[58]
VA-DSPME	Poly (HDDA)/ Graphene	None	REEs in Coal Fly Ash leachate 43-112%	Not reported	[59]
Ionic HDES-DLLME	Ionic (TBAC:oleic acid; 1:1)	Methanol (1.5 mL)	Organics pollutants/85-92%	–	[60]
HDES-LLME	DL-Menthol:formic acid; (2:1)	None	Cr(VI) in Food & Other samples/96.3-104%	AES Score: 72 & PP: 28 AGREE: 0.49 AGREEprep: 0.34	[61]
DLLME	Menthol:1-octanol (1:1.5)	None	Rhodamine-B 90.117%	WAC: 80.8 ComplexMoGAPI: 0.1/90	[62]

solvent was employed as the extraction medium for the recovery of samarium through the formation of the Sm-ARS complex. The proposed procedure offers a simple and solvent efficient approach to samarium extraction. Its analytical performance includes a linear working range of 30-150 μg L^{-1} and a limit of detection of 1.87 μg L^{-1} with an intra-day precision of 2.78% RSD. Recovery values of 99.0-100.5% in spiked magnet samples support the accuracy of the procedure for real-sample analysis. The use of a hydrophobic eugenol-based DES reduces dependence on conventional hazardous organic extraction solvents. The vortex-assisted extraction procedure requires a relatively small solvent volume and a short extraction time. These features simplify sample preparation and limit chemical waste generation. The environmental performance and practical applicability of the method were assessed using the AES and GAPI as well as the AGREE and BAGI. The AES score of 86 places the procedure in the excellent green category. The AGREE score of 0.65 and BAGI score of 62.5 provide further information on its environmental performance and practical suitability. The proposed method offers a laboratory-scale approach for samarium determination in waste Sm-Co magnets and may support the analytical evaluation of magnet recycling processes.

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CONFLICT OF INTEREST

The authors declare that there is no conflicts of interest regarding the publication of this article.

DECLARATION OF AI-ASSISTED TECHNOLOGIES

During the preparation of this manuscript, the authors used an AI-assisted tool(s) to improve the language and no data, results or scientific conclusions were generated by AI. All analyses, interpretations and conclusions are the authors' own. The authors reviewed and edited the content and take full responsibility for the published work.

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